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THE ACTION OF PERSPIRATION ON LEATHER*

Part I. The Action of Lactic Acid on Chrome Leather

By

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Summary

The constituents of perspiration most likely to damage chrome leather are lactic acid and sodium chloride. The factors affecting the extraction of chrome from leather by sodium lactate and sodium chloride solutions have been investigated.

The amounts of chrome extracted are dependent on the time and temperature of extraction but eventually an equilibrium is reached which is governed by the relative amounts of lactate and leather present. It is concluded that the system leather-sodium lactate solution behaves similarly to that of a cation exchange resin in a solution of metallic ions and anions capable of complexing with the metal. The effect of pH and different anions on the extraction are explained on this basis.

The distribution of chrome between leather and solution under standard conditions should serve as an indication of the relative stability of the chrome—collagen complex in different leathers and on this basis a procedure for testing the probable resistance of leathers to the detanning action of perspiration is suggested. So far little evidence has been obtained that the pH or basicity of tannage affects such resistance, though other factors may be of importance. It may be inferred that the higher the chrome content of the leather the longer will it withstand the action of the perspiration.

During stripping the shrinkage temperature of the leathers decreased progressively with the chrome content, all the chrome fixed apparently contributing equally to the hydrothermal stability.

Introduction

Perspiration is a potential source of damage to many types of leather articles, particularly to boot and shoe uppers, insoles and gloves. Not only may the constituents of perspiration cause damage to the leather, but the warm moist conditions associated with the production of perspiration may themselves be deleterious to the leather over long periods of time.

The chief constituents of perspiration are sodium chloride (0.3—0.5%), lactic acid (0.1—0.3%), amino acids (0.05%) and urea (0.05%)[1]. Smaller amounts of glucose, pyruvic acid and ammonia and a variety of bacteria and yeasts may also be present. On standing, urea is converted to ammonia by bacterial action and the alkalinity of the sweat increases, the pH values reported for sweat varying between 5 and 8[1].

It is now fairly generally agreed that chrome tanning involves the formation of co-ordination complexes between chromium and the carboxyl groups of the collagen[2], in some instances cross-links being formed between adjacent polypeptide chains in the protein. It has long been known that certain anions, particularly those containing carboxyl groups, have a detanning action on

* The work reported in this paper forms part of a research programme sponsored by the U.S. Department of Agriculture under the authority of U.S. Public Law 480.

chrome leather[3-6]. It is not unreasonable to assume that this detanning action is due to competition between the carboxyl groups of these anions and those of the protein for co-ordination with the chrome complexes. Anions of dicarboxylic and hydroxy acids which contain two groups capable of co-ordinating with chrome with the formation of relatively stable complexes are likely to be the most effective detanning agents. Simoncini[5] quotes the following order of effectiveness Tartrate > Oxalate > Citrate > Sulphate > Nitrate > Chloride and more recently Lollar[4] has reached similar conclusions.

The constituents of perspiration most likely to cause damage to chrome leather, therefore, are lactic acid and to a lesser extent sodium chloride. Gustavson[7] considers that the deleterious effect of perspiration is mainly attributable to the presence of lactates, but Colin-Russ[8] considers that the chloride is also responsible, for although ineffective as a detanning agent, it may, by reason of its relatively high concentration displace sulphate from the chrome complex.

Although the concentration of both lactic acid and sodium chloride in sweat are low, it is possible for these constituents to accumulate in the leather during wear. For example, profuse sweating for one hour could result in the accumulation of 0.5% sodium chloride and 0.3% lactic acid in a leather of average thickness. Roddy and Lollar[9] actually report the presence of 4 to 8% lactic acid in damaged areas of shoe uppers, together with appreciable amounts of soluble chrome. The detanning action of synthetic perspiration containing sodium lactate has also been demonstrated in laboratory tests simulating wear[10]. The action of perspiration on chrome and other types of leather has recently been reviewed by Seligsberger and Mann[11].

Although the detanning action of lactate is almost certainly due to the fact that it co-ordinates with the chromium at the expense of the carboxyl groups of the collagen, there is little information available regarding the factors affecting the rate and extent of the removal of chrome. For example, is all the chrome equally readily extracted or does the form in which the chrome is present in the leather influence the rate and extent of extraction? Such information my throw some light on the stability of the chrome-collagen complex and indicate methods of tanning and processing likely to produce leathers of maximum stability to moist heat, perspiration and other chemical reagents. It should also prove helpful in establishing a suitable method for testing leathers for their resistance to perspiration and to organic acids in general.

In the present paper the effect of time, temperature and concentration of lactate on the removal of chrome and on the shrinkage temperature of the leather have been studied. The effect of pH and the relative effect of different anions has also been examined.

Experimental Methods

Method of Extraction

The general procedure was to extract 1 g leather with 25 ml. solution in a stoppered conical flask.

The leather was cut into pieces about 0.5 cm. sq. and a strip 0.5 x 5 cm. for shrinkage temperature determination was included. In the initial experiments the flasks were shaken continuously in a water bath at the required temperature, but in later experiments they were placed in an incubator and shaken intermittently by hand. The times required to reach equilibrium were rather longer but the results were essentially the same.

After the required time of extraction the pieces were filtered off, washed with five 50 ml. portions of distilled water over a period of one hour and air dried. The pieces for shrinkage temperature were removed and the whole of the extracted samples taken for chrome determinations. When the chrome content of the extracted leather was likely to be less than 0.8 to 1.0%, 2 g leather or more were extracted with the appropriate volume of solution.

In most instances extractions were carried out at 50°C with 5% sodium lactate solution containing 5% sodium chloride. Except in the experiment designed to study the effects of pH, extractions were carried out at the pH of the sodium lactate solution—6.0. There was little change in pH during extraction; although the chrome leather is more acid than pH 6.0, the pH is not appreciably affected as the sodium lactate acts as a buffer in the pH range 2 to 6.

CHROME. Chrome was determined by oxidation with perchloric acid and titration with ferrous ammonium sulphate[12].

NITROGEN. The nitrogen in the extracts was determined by a microkjeldahl procedure[13].

SHRINKAGE TEMPERATURE. The leather was soaked back in water under reduced pressure and the shrinkage temperature determined in water or, if above 100°C, in 75% v/v glycerol water mixture, density 1.194. The rate of heating was 1 to 2°C per min. and the shrinkage temperature was taken as the point at which any reduction from the maximum length was first observed.

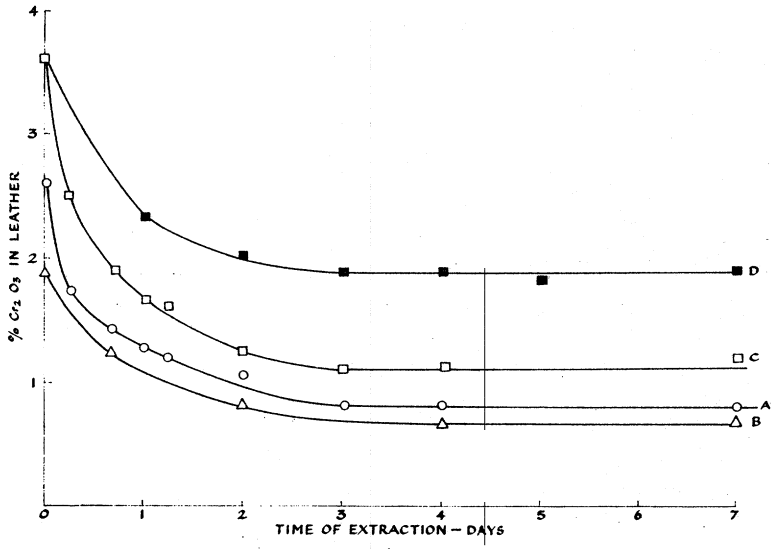
TRYPTIC DIGESTION. The extracted leather was cut into small pieces about 2 mm. sq. and 300 mg. samples treated with 25 ml. 0.05% crystalline trypsin (B.D.H.) in 0.15 M boric acid-sodium borate buffer pH 8.08 for 3 hrs. at 50°C. The solution was filtered and the dissolved nitrogen determined. The results were expressed as g. hide substance dissolved as a per cent of the air dry extracted leather. The factor 5.62 was used for conversion of nitrogen to hide substance.

Experimental Results

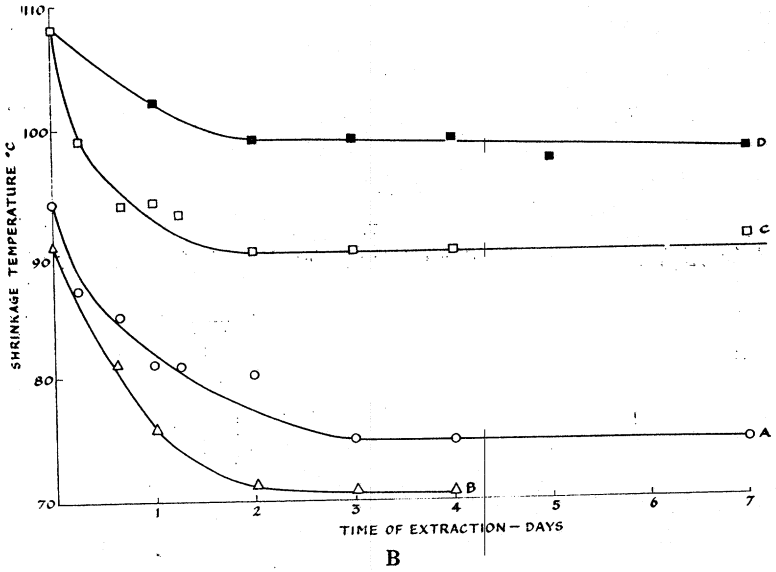
EFFECT OF TIME AND TEMPERATURE OF EXTRACTION

Chrome leather prepared from cape-type sheepskins was used for these experiments. Some leathers were chrome tanned only and others were fatliquored and dyed (see footnote to Table 1). 5% or 2.5% sodium lactate solutions containing 5% sodium chloride were used and the extraction carried

out at 50°C for periods up to 8 days. With one of the leathers extractions were also carried out at 20°, 30°, 40°, 60° and 70°C.



A



B

FIG. 1.

Decrease in chrome content (A) and shrinkage temperature (B) with time in sodium lactate solutions containing 5% sodium chloride.

Leathers from Series III—Table I.

A Leather 4 „ „ 5% lactate.
B „ 5 „ „ „ „
C „ 6 „ „ „ „
D „ 6 „ „ 2.5% lactate.

With all the leathers tested the chrome content and shrinkage temperature fell rapidly during the first two or three days and then there was little further decrease over the periods of extraction examined. Typical curves relating chrome content and shrinkage temperature with time of extraction are given in Fig. 1.

The removal of chrome from the leather appears to take place smoothly and there are no inflexions in the curves which can be related to the removal of more loosely bound chrome. The shrinkage temperature also decreased in the same manner as the chrome content and there is no indication that the chrome extracted in the early stages behaves any differently from the rest with respect to its contribution to hydrothermal stability. The curves obtained with 2.5 and 5% sodium lactate solutions are similar in shape but the amounts of chrome extracted and the fall in shrinkage temperature are less with the lower concentration.

The chrome contents and shrinkage temperatures of a number of leathers after extraction for 4 or 8 days are recorded in Table I. The values appear to be mainly dependent on the initial chrome content of the leather and the concentration of lactate used and do not appear to be affected by the conditions of tanning covered. There is, perhaps some indication that high final pH values in tanning are associated with greater retention of chrome.

The effect of temperature on the extraction is illustrated in Fig. 2. The removal of chrome followed essentially the same course at 40, 50 and 60°C, though the time taken to reach equilibrium decreased slightly with increase in temperature. At 20°C and 30°C the extraction was much slower and equilibrium was not reached in sixteen days. The equilibrium chrome content was appreciably lower at 70°C than at 60°C, presumably because the leather begins to shrink. The shrinkage temperature also decreased very sharply at 70°C and after one day shrinkage began to take place during the treatment. This also occurred after 2 days at 60°C. It seems that when shrinkage temperature falls to within about 10°C of that at which the extraction was made slow shrinkage begins to take place.

Effect of Concentration of Lactate

Chrome tanned sheepskin leather was extracted with sodium lactate solutions of various concentrations in the range 0-16%. The extractions were carried out at 50°C for 8 days using 25 ml solution per gram of leather. The chrome content of the solutions and of the washed leather were determined.

The chrome extracted increased with the concentration of lactate and an approximately linear relationship was found between the concentration of lactate and the ratio of chrome extracted to that remaining in the leather.

Within limits, reducing the volume of lactate solution decreases the chrome extracted in a similar manner. In more general terms

$$\frac{\text{Chrome in solution}}{\text{Chrome remaining in leather}} = K. \frac{\text{concentration of skin}}{\text{concentration of lactate}}$$

TABLE I

Loss of Chrome and Fall in Shrinkage Temperature on Treatment in 5% Sodium Lactate Solutions

Description of Leather		Chrome Contents Cr_2O_3 as % moisture free leather Initial	After Extraction	% Retained After Extraction	Shrinkage Temperature °C Initial	After Extraction	% of Initial Value
Series I—Blue Crust Leathers Unmasked Tannage							
Chrome offered on skin weight	Final pH of tannage						
3.1%	3.5	2.04	0.64	31	98	79	80
	4.0	2.15	0.89	41	100	78	78
	4.5	2.62	0.90	34	106	80	76
6.2%	3.5	3.74	1.37	37	108	90	83
	4.0	4.08	1.52	37	109	90	83
	4.5	5.01	2.32	46	113	96	85
12.5%	3.5	5.44	2.21	41	114	96	84
	4.0	6.15	2.41	39	115	97	84
	4.5	8.62	5.46	63	117	102	90
25%	3.5	6.95	2.55	37	117	98	84
	4.0	8.53	3.45	40	119	101	85
	4.5	11.46	5.99	52	122	105	86
Series II—Blue Crust Leathers Unmasked Tannage							
Initial Basicity	0%	2.22	0.32	14	108	82	76
Final pH	3.5	1.65	0.40	24	106	79	75
Initial Basicity	0%	3.97	1.05	26	112	83	74
Final pH	4.8	2.59	0.40	15	109	79	73
Initial Basicity	40%	3.68	0.76	21	115	91	79
Final pH	3.5	2.68	0.61	23	109	79	73
Initial Basicity	40%	4.32	0.71	17	118	83	71
Final pH	4.8	3.29	0.75	23	113	81	72
Series III—Leathers after fat liquoring							
1. Unmasked tannage Final pH	3.5	4.27	1.80	42	104	72	69
2. Commercial leathers undyed		1.97	0.60	30	97	70	72
3.		4.77	1.41	30	114	87	76
4. Formate masked tannage		2.61	0.80	31	94	75	80
5. Final pH	3.6	1.86	0.65	35	90	68	76
6. Dyed		3.59	1.18	33	108	90	83

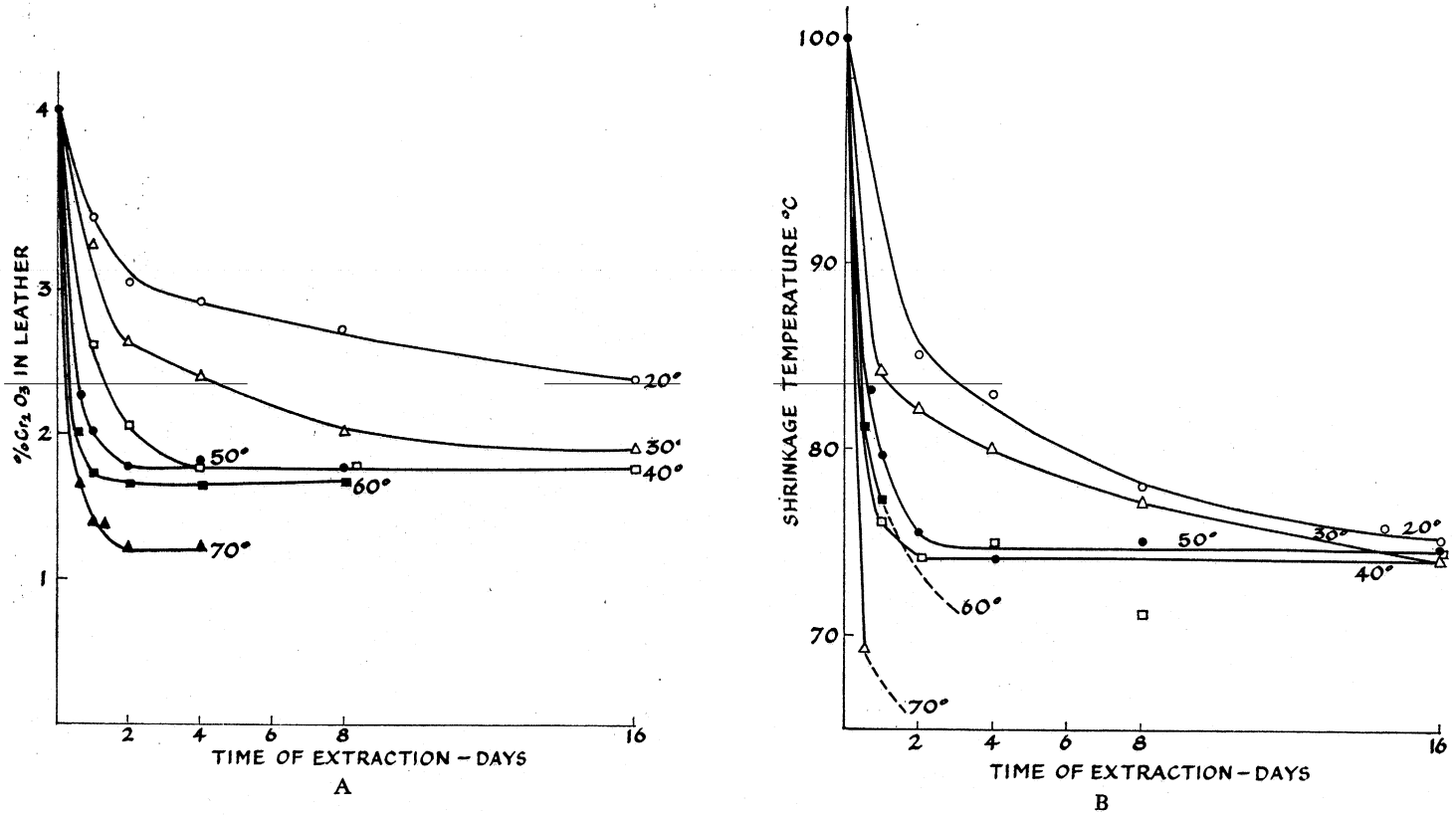


FIG. 2.

The effect of temperature on the extraction of chrome and the fall in shrinkage temperature or leathers treated in 5% sodium lactate—5% sodium chloride solutions.

It seems, therefore, that the chrome is distributing itself between the skin and the solution according to the number of groups present in each capable of complexing with chrome. Using 25 ml 5% sodium lactate solution for 1 g leather the number of carboxyl groups in solution due to the lactate is seven to eight times that of the protein carboxyl groups in the leather, whereas the distribution of chrome in solution and leather is of the order of 2 to 1. The collagen-chrome complex would, therefore, appear to dissociate to an appreciably smaller extent than the corresponding lactate-complexes.

In a further experiment the effect of damping the leather with a given volume of concentrated lactate solution and storing in a polythene bag at 50°C was compared with extraction with the same amount of lactate in a large volume of solution. In each case the leather was thoroughly washed to remove chrome loosened during the treatment. Moistening the leather with the more concentrated solution was found to have rather more effect than extraction with the dilute solution.

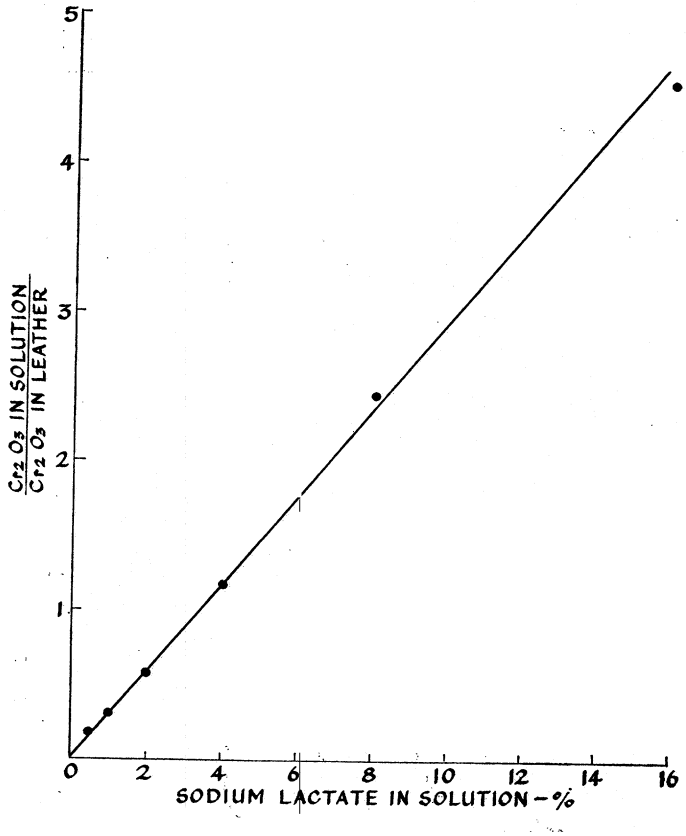


FIG. 3.

Relationship between chrome extracted and concentration of sodium lactate solutions.

Successive Extraction of Chrome Leather

Further experiments were carried out to see whether the proportion of chrome extracted was the same in each of a number of successive extractions. Samples of the leather were extracted one to five times with 2% sodium lactate solutions, the leathers being washed in the usual way between each. The chrome content of the leather was determined after each extraction and the percentage chrome retained in each extraction calculated (see Table 2). With the majority of leathers tested the percentage chrome retained by the leather in the first extractions varied between 40 and 50%. In further extractions the proportions of chrome retained by the leather increased and after two or three extractions became approximately constant between 60 and 70%.

TABLE II

Successive Extraction of Chrome Leather with 2% sodium Lactate Solution

Initial	Chrome contents of leather after extraction. Cr_2O_3 on moisture free weight. Extractions					% Chrome retained in each extraction. Extractions				
	1st	2nd	3rd	4th	5th	1st	2nd	3rd	4th	5th
2.94	1.52	1.10	0.76	—	—	52	72	69	—	—
4.93	2.17	1.16	0.64	0.38	—	44	53	55	60	—
3.74	1.46	0.68	0.47	—	—	39	47	69	—	—
4.08	1.51	0.89	0.52	0.34	0.22	37	58	59	65	67
5.01	2.06	1.48	1.04	—	—	41	72	70	—	—
5.44	2.87	1.30	0.78	0.50	—	53	45	60	64	
6.15	2.51	1.57	0.94	0.61	—	41	63	60	65	
6.95	3.15	1.64	0.98	0.65	—	45	52	60	66	
8.53	4.03	2.14	1.34	0.86	—	47	53	63	64	

The percentages of chrome removed in the early extractions and to a lesser extent in the later extractions varies with the leather; these differences do not seem to be related to the initial chrome content or to the final pH of the tannage. The fall in shrinkage temperature during the extraction fell in accordance with the chrome content, and there was no indication that the chrome removed in the first extractions had any less influence on the hydrothermal stability than that retained in the later extracts.

Effect of pH

On the basis of the previous results increases in acidity should lead to removal of chrome from the leather, the chromium combined with carboxyl groups being displaced in this case by hydrogen ions. In the presence of lactate, however, increase in hydrogen concentration will reduce the effectiveness of the lactate since an increasing proportion of this will be present in the non-ionised form. Increases in pH value above about 6.0 will also reduce the chrome fixed, since the hydroxyl ions will tend to replace carboxyl groups in the chrome complex in a similar manner to lactate ions.

The influence of pH on the extraction of chrome from leather in the presence of sodium lactate and sodium chloride has, therefore, been followed in order to obtain some information regarding the magnitude of these effects.

As the chrome content decreases the susceptibility of the leather to hydrolytic and bacterial action will tend to increase. In this experiment an attempt has been made to assess this by determining the loss of protein during the extraction and the susceptibility of the extracted leather to the action of trypsin.

Two undyed chrome leathers prepared from cape-type sheep skins of chrome contents 2.9 and 4.9% were used. Two gram samples of leather were extracted with 50 ml of each of the following solutions for 4 days at 50°C.

(1) 5% sodium chloride
(2) 4% sodium lactate+5% sodium chloride
(3) 8% sodium lactate+5% sodium chloride

Extractions were carried out in triplicate over the pH range 2.0 to 10.0. The solutions below pH 4.0 were prepared from lactic acid and those above 4.0 by the addition of hydrochloric acid or sodium hydroxide to solutions of sodium lactate. Additions of acid or alkali were made during the extractions to maintain the pH as far as possible at the required values. For pH values above 7.0 and below 5.0 it was necessary to add relatively large amounts of acid or alkali. The leather of the lower chrome content was extracted before this was fully realised and the more extreme pH values were not maintained.

Extraction of Chrome and Fall in Shrinkage Temperature

The results are summarised in Figs. 4 and 5. In sodium chloride solutions little chrome was extracted at pH 5.0 and above, but there was an appreciable fall in shrinkage temperature. Presumably, although the hydroxyl ions caused some displacement of chromium from protein groups, this was not necessarily extracted but was precipitated as a basic salt. The fall in shrinkage temperature was probably also due to replacement of sulphate ions in the chrome complex by chloride ions. As the pH fell from 5 to 2 there was a rapid increase in the amounts of chrome extracted until at pH 2.0 about 50% was removed. This increased extraction must be almost entirely due to displacement of chromium by hydrogen ions. The shrinkage temperature fell in a corresponding manner.

The presence of sodium lactate caused large amounts of chrome to be extracted at all pH values. The increased extraction with fall in pH was less marked than with sodium chloride alone. It would seem, therefore, that the increased hydrogen ion concentration is largely compensated for by the reduced amounts of lactate in the ionised form and, hence, not available for complexing with chrome. The pK of lactic acid is 3.8 and, in water at pH 3.0 approximately 90% of the lactate will be present as the undissociated acid[14]. At pH values above 6.0 there was an increase in the amounts of chrome extracted and a corresponding fall in shrinkage temperature. Chrome

displaced from the protein by hydroxyl ions will be less readily precipitated as a basic salt in the presence of lactate ions than in sodium chloride alone.

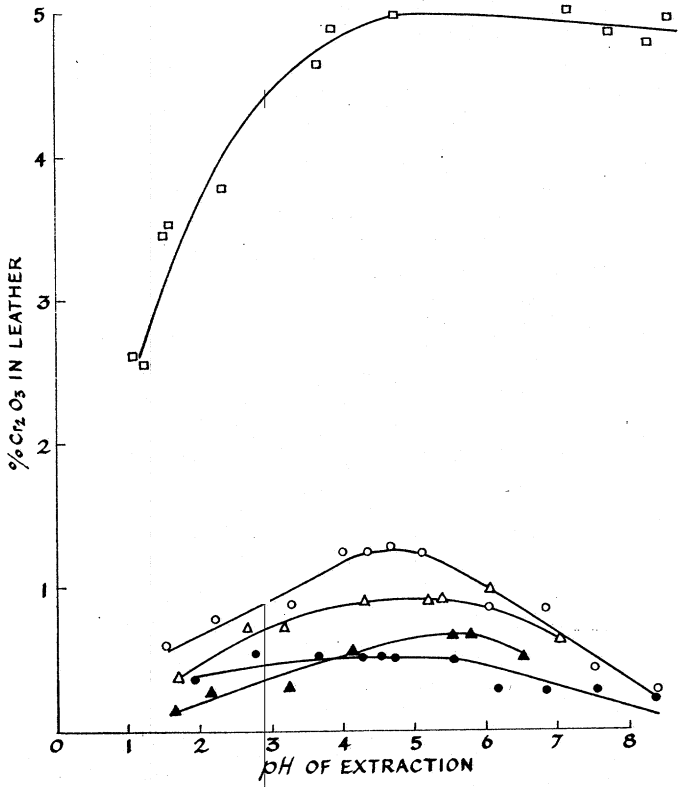


FIG. 4.

Chrome content of leather samples after extraction with sodium lactate and sodium chloride solutions at various pH values.

○ 4% sodium lactate—5% sodium chloride.
● 8% „ „ „ „ „
□ 5% sodium chloride.

Leather of initial chrome content 4.9% and shrinkage temperature 116°C.

△ 4% sodium lactate—5% sodium chloride.
▲ 8% „ „ „ „ „

Leather of initial chrome content 2.9% and shrinkage temperature 101°C.

DEGRADATION OF THE PROTEIN

The solubilisation of protein during the extraction and on subsequent digestion of the leather with trypsin is shown graphically in Figs. 6 and 7. In sodium chloride solutions loss of hide substance during the extractions was negligible at all pH values (less than 0.1% between 4 and 7, 0.2% at pH 2.0 and only 0.3% at pH 9.0).

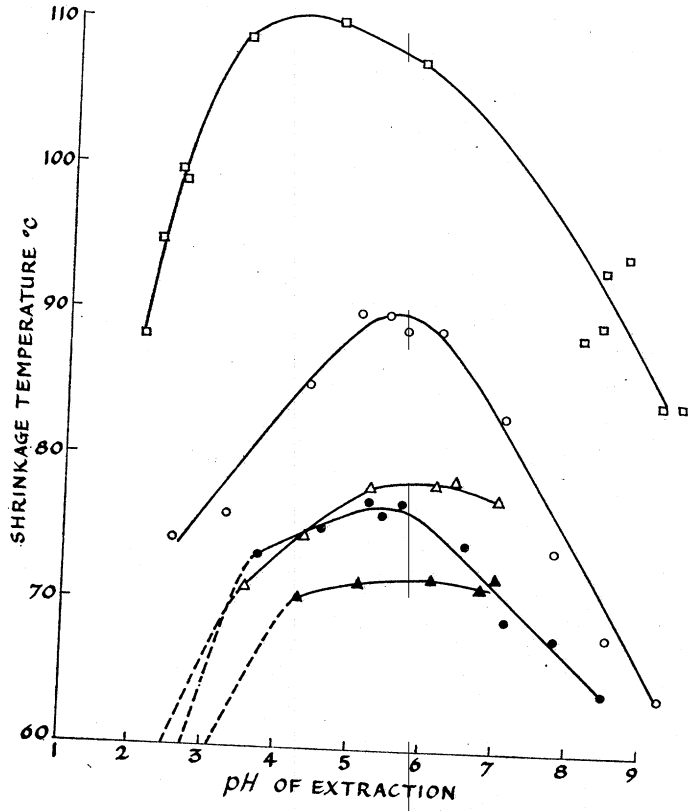


FIG. 5.

Shrinkage temperature of leather samples after extraction with sodium lactate and sodium chloride solutions at various pH values. For legends see Fig. 4.

The amounts of protein dissolved during extraction with lactate and on subsequent digestion with trypsin were dependent both on the pH of the extraction and on the level to which the chrome content was reduced. In the pH range 4 to 7 little protein was dissolved, even when the chrome content was reduced to between 1.0 and 0.5% but as the pH of the extraction was increased above 7.0 or reduced below 4.0 the amounts dissolved increased sharply. Under these conditions the protein dissolved was greatly affected by the extent to which the chrome content had been reduced. For example, following extraction at pH 3.0 only about 3.0% hide substance was digested by trypsin from a sample whose chrome content had been reduced to 0.6%, whereas about 25 and 50% were digested from samples of chrome content 0.4 and 0.2% respectively.

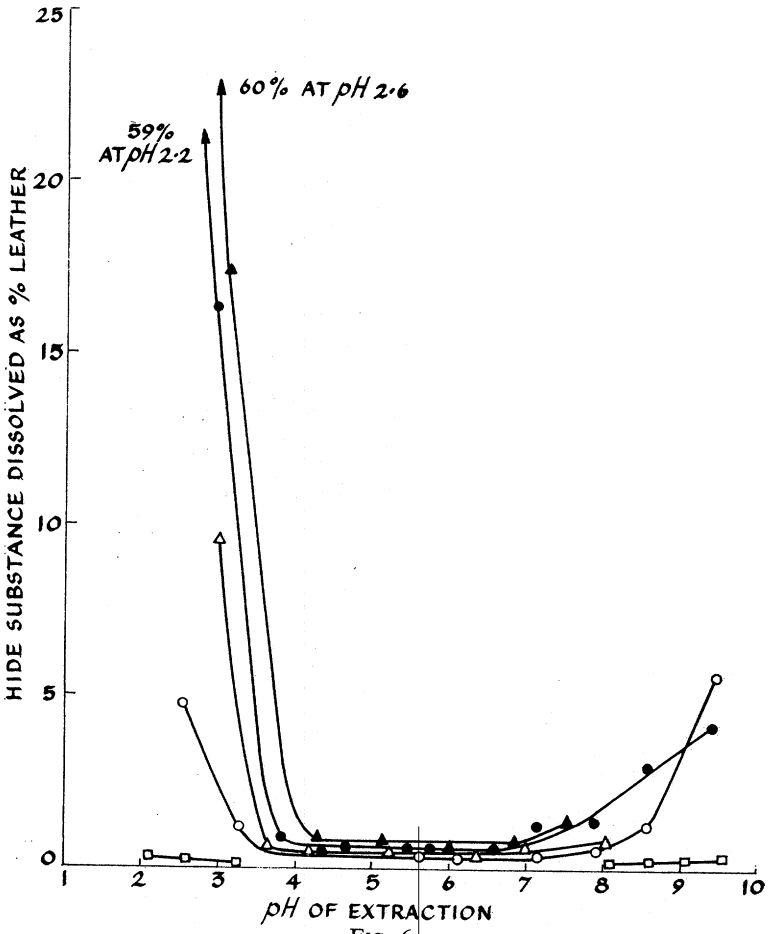


FIG. 6.

Hide substance dissolved during extractions with sodium lactate and sodium chloride solutions at various pH values—for legends see Fig. 4.

The direct influence of the pH of extraction on digestion with trypsin, apart from its effect on the chrome content, is illustrated by the varying amounts of protein digested from samples whose chrome contents had been reduced to 0.3% by extraction at pH 3, 4 and 8 respectively, namely, 50, 10 and 20%.

EFFECT OF DIFFERENT ANIONS

The extraction of chrome by a variety of salts chiefly those of organic acids, by surface active agents, such as might be used in mordants and fat liquors, and by dyes has been investigated.

Samples of leather were extracted with 0.5N solutions of the salts or 4% solutions of the other materials for 8 days at 50°C (see Table 3). The pH was adjusted to between 5 and 6 in all cases and maintained in this range. Extractions were carried out in duplicate.

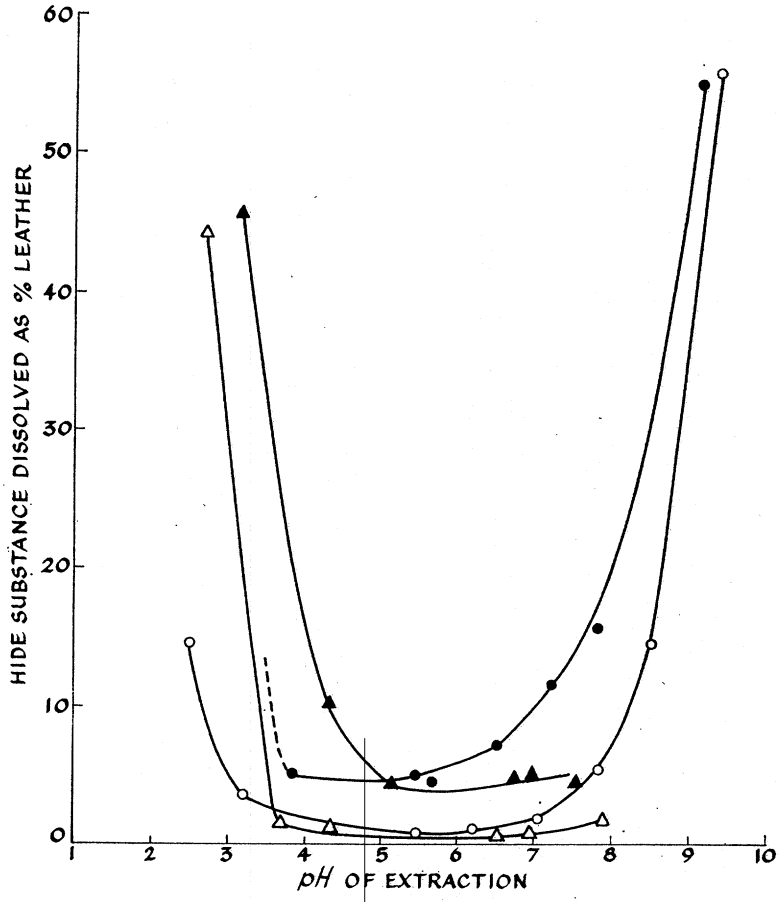


FIG. 7.

Hide substance dissolved by Trypsin digestion following extraction by sodium lactate and sodium chloride solutions at various pH values—for legends see Fig. 4.

As would be expected on general principles salts of the organic acids, and particularly the hydroxy and dicarboxylic acids, were the most effective as stripping agents. The action of sodium chloride in reducing the shrinkage temperature without appreciably reducing the chrome content was again observed. The effectiveness of the various anions in extracting chrome increased in the following order—$Cl = SO_4 <$ formate $<$ acetate $<$ amino acetate $<$ lactate $<$ tartrate $<$ citrate, oxalate. Urea had no effect and ethylene diamine tetraacetic acid was rather less effective than oxalate. None of the surface active agents had any appreciable effect except that the anionic fat liquor tended to reduce the shrinkage temperature slightly. Malachite green and to a lesser extent Kiton red reduced the chrome content and shrinkage temperature.

TABLE 3

The Stripping Action of Various Salts and other substances on Chrome Leather

Stripping Agent	Concentration	Chrome Content after stripping % Cr_2O_3	Shrinkage Temperature after stripping °C
None	—	2.45	113
Sodium Salts			
Sulphate	N	2.3	110
Chloride	0.5N	2.3	101
Formate	„	2.1	106
Acetate	„	1.7	95
Lactate	„	0.4	68
Oxalate	„	0.1	69d
Tartrate	„	0.2	66
Citrate	„	0.1	67d
Amino Acetate	„	0.9	90
Ammonium Chloride	„	2.3	109
Urea	N	2.4	108
Ethylene diamine-tetra-acetate	O.5N	0.1	66d
Cationic Sperm Oil	4%	2.1	109
Anionic Sperm Oil	„	2.4	106
Nonionic Sperm Oil	„	2.2	110
Teepol	„	2.3	110
Lissolamine A	„	2.2	110
Corilene D.G.	„	2.4	111
Kiton Red	„	2.2	105
Malachite Green	„	1.7	104
Bismark Brown	„	2.3	108
Neolan Red R.E.G.*	„	4.8	114

* Contains Chromium.

d=appeared damaged, some shrinkage had probably occurred during the stripping.

Discussion

It is clear from these results that appreciable amounts of chrome are extracted from leather by sodium lactate solutions and these losses are accompanied by considerable decreases in shrinkage temperature. The amounts of chrome removed are dependent on time and temperature but eventually an equilibrium is set up which is dependent almost exclusively on the amount of lactate present in relation to the leather weight.

It seems that the system leather-sodium lactate solution is similar to that of a carboxylic cation exchange resin in a solution containing metallic ions and anions capable of complexing with the metal. At equilibrium the chrome is distributed between the skin and the solution according to the number of groups present in each phase with which it is able to co-ordinate and its relative affinity for these. The effect of pH on the extraction of chrome is readily explained on this basis, the hydroxyl ions compete with the carboxyl ions for chromium in the same way as lactate ions, while hydrogen ions

have a double effect, displacing chromium from both protein and lactate carboxyl groups, the net effect being dependent on the dissociation constants of the two acid groups.

It may be assumed that the number of groups in the skin capable of co-ordinating with chrome does not vary greatly from one leather to another and hence the distribution of chrome between leather and solution at equilibrium under standard conditions should serve as an indication of the relative stability of the chrome-collagen complex and hence of the probable resistance of leather to the detanning action of perspiration.

Chrome may be present in the leather in a variety of ways, i.e. bound to one carboxyl group (unipoint fixation), to two or more carboxyl groups (multipoint fixation)[2], bound as an anionic complex to other groups in the protein or merely present as a basic complex precipitated or loosely associated with the protein fibres. One might expect these to have different affinities for the protein and, hence, to be more or less readily extracted by lactate. The results of tests carried out so far show little indications of such differences although they include leathers tanned at various pH values and basicities and in masked and unmasked liquors (see Table 1). In successive extraction of the same leather higher proportions of chrome were removed in the earlier extractions than in the later ones. All the chrome leathers behaved similarly with respect to hydrothermal stability however, the shrinkage temperature decreasing regularly with the chrome content.

It is clear from these results that the lactate present in perspiration is likely to lead to displacement of chrome from the leather. This loosened chrome may then be washed out or migrate to other parts of the leather during flexing, or to the surface during evaporation of moisture from the leather. The extent of the detannage will depend on the amount of perspiration absorbed by the leather, and whether this is subsequently washed out of the leather or not is immaterial.

It may be inferred that the higher the chrome content of the leather the longer will it withstand the action of perspiration. Although some changes in properties may occur, it will be some time before the chrome content is reduced sufficiently to allow extensive bacterial or hydrolytic action to occur. The results suggest that such degradation is likely to become apparent when the chrome content falls below about 1%. Although so far there has been little indication that the resistance of chrome leathers to the action of lactate solutions is appreciably influenced by the conditions of tanning, it is possible that other factors not yet studied may affect this. There is, for example, a slight difference between the leathers in Series I and II and Table 1. In both series unmasked chrome liquors containing sodium sulphate were used but in Series I the tannages were carried out over a relatively long period of time and the leathers were neutralised with sodium bicarbonate, whereas in Series II the tannages were more rapid and tap water was used for neutralisation.

On the basis of the results obtained in this investigation the following procedure for testing chrome leathers has been adopted. 1 g leather is extracted with 25 ml of a solution containing 5 g sodium lactate and 5 g sodium chloride per 100 ml for 4 days at 50°C followed by washing with 5 × 50 ml water. This solution represents a 10–15 fold concentration of perspiration. The chrome remaining in the leather is then expressed as a percentage of the original chrome content. The shrinkage temperature of the extracted leather is also determined. In wear the perspiration accumulates in the leather and it might be argued that a more direct indication of the resistance of a leather to perspiration might be obtained by repeated damping of the leather with a given volume of lactate or other solution resembling perspiration followed by incubation at 40 or 50°C. In practice, however, it was found extremely difficult and tedious to apply a given volume of a concentrated solution of perspiration to a piece of leather and ensure that it was evenly distributed. Provided the same amount of lactate was used for a given weight of leather and the leather was washed to remove solubilised chrome, similar results were obtained by immersion of the leather in a given volume of more dilute solution and it has been found more convenient to adopt this method. The appearance and fibre structure of leather treated in this way is similar to that of leather damaged by perspiration.

Finally, some comment should be made regarding the significance of the results obtained on the effect of pH. Increase in pH above 7.0 or decrease below 4.0 leads to increased displacement of chrome and fall in shrinkage temperature and in the extreme to degradation of the protein. The pH values recorded for perspiration usually lie between 6 and 7[1] and on standing the pH value may increase to 8 or 8.5. Perspiration, therefore, will not cause the pH of the leather to fall below 4.0. It is possible, however, that it may raise the pH of some chrome leathers above 7.0. In 100 hours profuse sweating, up to 10 ml perspiration per sq. cm. of body surface may be produced[15]. If all the urea in this is converted to ammonium carbonate it would be equivalent to about 1.5 ml O.1N alkali and assuming a leather of average thickness this would amount to nearly 5.0 ml per g. of leather, sufficient to raise the pH of some leathers appreciably.

The effect of low pH values on the removal of chrome is of some interest with respect to the dyeing of chrome leathers and points to the desirability of controlling the pH at as high a value as possible. The advantages of using a weak acid to facilitate this control must be weighed against the effect of the anion of the acid on the extraction of chrome. Hydroxy and dicarboxylic acids such as citric, lactic and oxalic should obviously be avoided but the use of an acid such as formic, which does not greatly increase the extraction of chrome, may be justified by the more efficient control of pH which results from its use.

Acknowledgment

Thanks are due to Mrs. A. Dexter and Mr. P. Whitehead for technical assistance. Also, to the U.S. Department of Agriculture and the Council of

the British Leather Manufacturers' Research Association for permission to publish this paper.

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Received March 9th, 1960.

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